Wastewater to Drinking Water: Are emerging contaminants making it through?

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INTRODUCTION

Lake Mead serves as the primary drinking water source for Las Vegas, NV and surrounding communities. Besides snow-melt from the Rockies, water levels are supplemented by the inflow of treated wastewater from communities along the Colorado River, including Las Vegas. This use-reuse practice is becoming commonplace in the arid Southwest and begs the question are organic contaminants, originating in the wastewater, ending up in the drinking water?

In 2005, a study was conducted using passive sampling devices (SPMDs and POCIS, Figure 1) to track the occurrence of trace amounts of organic wastewater contaminants (OWCs including pharmaceuticals and personal care products, pesticides, industrial chemicals) characteristic of wastewater treatment plants (WWTPs) at two sites in Las Vegas Wash, one site near Hemingway Harbor in Lake Mead, and in finished drinking (tap) water within the City of Las Vegas.

STUDY DESIGN

One canister of SPMDs and three canisters of POCIS were deployed at three surface water sites and plumbed into a drinking water supply in the City of Las Vegas for 35 days between January and February of 2005.

The sites selected included (Figure 1):

- Las Vegas Wash #1 (LVW1), near USGS stream gage, immediately downstream of the convergence of the City of Las Vegas and Clark County WWTPs
- Las Vegas Wash #2 (LVW2), downstream of Northshore Rd bridge (Hwy 147) accessed from the Wetland Trail overlook parking lot
- Hemingway Harbor in Lake Mead (HH), deployed from the end of the handicap fishing pier
- Drinking Water in Las Vegas (DW), tap water flowed through an enclosed sampling chamber in a laboratory in the City of Las Vegas

SPMDs were analyzed for: PAHs (34), organochlorine pesticides (34), Total PCBs

POCIS were analyzed for: agricultural pesticides (26), hormones (4), pharmaceuticals (9), and OWCs (50).

POCIS extracts were also screened for estrogenic activity using the yeast estrogen screen (YES assay). A toxicity identification and evaluation (TIE) approach was also used to isolate and identify estrogenic chemicals.

In total, 158 chemicals or chemical classes were targeted in this study.

PROCESSING AND ANALYSIS OF PASSIVE SAMPLERS

The processing and analysis for the SPMDs and POCIS followed published procedures (Alvarez et al., 2008a, 2008b; Jones-Lepp et al., 2004, Figure 2).

In general, each field and quality control sample was processed using class-specific cleanup and fractionation schemes (i.e., size exclusion chromatography, Florisil®, silica gel, reactive silica gel, solid-phase extraction). Analyses were performed using either a gas chromatograph with a mass selective detector (GC-MSD) for agricultural pesticides, PAHs, OWCs, hormones, and TIE-YES extracts; GC with an electron capture detector (GC-ECD) for PCBs and organochlorine pesticides; or a HPLC with an ion trap mass spectrometer (LC-ITMS) for pharmaceuticals.

Samples designated for the YES were screened prior to rigorous cleanup to prevent removal of unknown but bioactive (estrogenic) chemicals.

Samples for the TIE-YES were fractionated on silica gel into 7 fractions which were screened by the YES in duplicate. Portions of fractions which gave a positive estrogenic response were analyzed by full-scan GC/MS. Tentative identification was achieved by comparison of unknown mass spectra to a NIST MS library. Identifications were confirmed if authentic reference standards were available.

Figure 1. Surface water and treated drinking water sampling site locations within the Lake Mead and Las Vegas, NV vicinity.

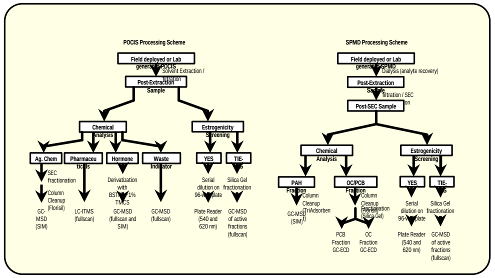

Figure 2. Flowchart of the processing and analysis steps of the passive samplers.

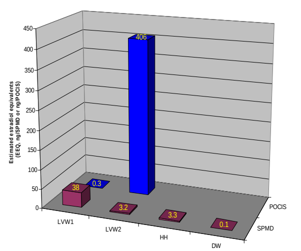

Figure 3. Estimated estradiol equivalents expressed as ng of 17ß-estradiol per sampler (SPMD or POCIS).

Table 1. Estimated water concentrations of chemicals detected in the passive samplers.

Chemicals Measured in SPMDs

OC Pesticides	LVW1 ng/L	LVW2 ng/L	HH ng/L	DW ng/L
Trifluralin	0.07	0.13		0.07
Hexachlorobenzene	0.26	0.24	0.02	0.02
Pentachloroanisole	0.17	0.19	0.01	*0.00*
alpha-Benzenehexachlorid	*0.06*	0.41	*0.06*	*0.07*
beta-Benzenehexachloride	*0.05*	1.10	0.09	0.06
delta-Benzenehexachloride	0.12	0.23	*0.07*	*0.07*
Lindane	0.48	0.46	0.16	0.10
Dacthal	0.09	0.16	0.10	0.06
Chlorpyrifos	0.50	0.41	*0.036*	
cis-Chlordane	0.08	0.15	0.02	*0.01*
trans-Chlordane	0.07	0.12	*0.01*	*0..8*
cis-Nonachlor	0.01	0.03	0.01	*0.003*
trans-Nonachlor	0.03	0.06		
Oxychlordane	0.00	0.03	*0.003*	
Heptachlor	0.01	*0.00*		
Heptachlor Epoxide	0.20	0.02	*0.02*	*0.30*
o,p'-DDE		0.13	0.03	0.02
p,p'-DDE	0.05	0.34	0.11	0.06
o,p'-DDD	0.04	0.14	0.04	0.02
p,p'-DDD		0.13	0.05	*0.02*
o,p'-DDT	0.53			
p,p'-DDT	0.06	0.09	0.02	0.02
Dieldrin	0.14	0.30	0.04	0.01
Endrin	0.02	0.07	0.02	0.01
p,p'-Methoxychlor		*0.04*	<0.13	
Mirex		0.14		
cis-Permethrin		0.04	0.09	

OC Pesticides and PCBs	LVW1 ng/L	LVW2 ng/L	HH ng/L	DW ng/L
Endosulfan	2.0	1.90		
Endosulfan-II	3.8	3.9		
Endosulfan Sulfate	1.0	1.10	0.18	*0.02*
Total PCBs	1.3	1.7		
PAHs	ng/L	ng/L	ng/L	ng/L
Acenaphthene	*0.10*	0.21		
Fluorene	0.22	0.32		
Phenanthrene	2.8	2.5	0.47	0.46
Anthracene	0.27	0.25		
Fluoranthene	0.83	1.3	*0.12*	*0.11*
Pyrene	1.4	2.5	*0.23*	
Chrysene	*0.42*	0.41		
Benzo[b]fluoranthene		*0.06*		
Benzo[a]pyrene	*0.05*	*0.04*		
2-methylnaphthalene		1.2	0.65	0.32
1-methylnaphthalene		0.70	0.32	
1-ethylnaphthalene		0.16	0.17	
1,2-dimethylnaphthalene		0.20		
4-methylbiphenyl	*0.17*		*0.18*	
2,3,5-trimethylnaphthalene			0.12	
1-methylfluorene			*0.48*	
Dibenzothiophene		0.16		
2-methylphenanthrene	1.8	2.1		
3,6-dimethylphenanthrene	0.58	0.81		
2-methylfluoranthene		0.13		
Benzo[b]naphtho[2,1-d]thiophene	0.17	0.20		
Benzo[e]pyrene	0.10	0.12		

Chemicals Measured in POCIS

Prescription Drugs	LVW1 ng/L	LVW2 ng/L	HH ng/L	DW ng/L
17a-Ethynylestradiol		*3.6*		
Azithromycin	0.4	0.5		
Illicit Drugs	ng/L	ng/L	ng/L	ng/L
Methamphetamine	9.3	6.7		
MDMA (Ecstasy)	0.3			
Agricultural Pesticides	ng/L	ng/L	ng/L	ng/L
Terbuthylazine	11	42	1.0	
Flame Retardants *	ng/POCIS	ng/POCIS	ng/POCIS	ng/POCIS
Tri(2-chloroethyl) phosphate	930	1100		*85***
Tributyl phosphate	620	1000		*25***
Tri(dichloroisopropyl) phosphate	990	1400	*50*	
Tri(butoxyethyl) phosphate	1100	1290		240**
Triphenyl phosphate	210	110		
Plasticizers *	ng/POCIS	ng/POCIS	ng/POCIS	ng/POCIS
Diethylphthalate	[illegible]	[illegible]		[illegible]
Diethylhexylphthalate (DEHP)	*1400*			*930***

Prescription/Nonprescription Drugs *	LVW1 ng/POCIS	LVW2 ng/POCIS	HH ng/POCIS	DW ng/POCIS
Clindamycin	34			
Pseudoephredrine	4	7		
Waste Indicator Chemicals *	ng/POCIS	ng/POCIS	ng/POCIS	ng/POCIS
para-Cresol	17000	640	9200	1700**
N,N-diethyltoluamide (DEET)	390	360	*50*	*40***
Ethyl citrate	430	340		
N-butyl benzenesulfonamide	2200	2100	120	430**
Caffeine	330	240		
Benzophenone	160	100	*20*	*30***
Cholesterol	*380*	2100	*600*	930**
Fragrances *	ng/POCIS	ng/POCIS	ng/POCIS	ng/POCIS
Celestolide (ADBI)	*50*			
Phantolide (AHMI)	130	*90*		
Traseolide (ATII)	160	*90*		
[illegible]	9600	8600		
Tonalide (AHTN)	1900	1300		
Musk Ketone	[illegible]	[illegible]		

Chemical groups designated with a * are reported as ng of chemical per sampler as determination of the estimated water concentrations was not possible due to a lack of sampling rate information for that chemical.

Values in *italics* are estimated values below the method quantitation limit.

NA = sample analysis not completed.

** Results from the DW POCIS samples are an average of the extracts from two POCIS.

ESTROGENIC ACTIVITY OF SAMPLED CHEMICALS

Yeast Estrogen Screen (YES assay) – *in vitro* test for estrogenic activity

Both LVW1 and LVW2 POCIS samples were positive indicating the presence of estrogenic chemicals with estimated estradiol equivalent (EEQ) concentrations of 0.28 ng/L (LVW1) and 26 ng/L (LVW2). The HH and DW samples were not estrogenic (Figure 3). The SPMDs showed the greatest estrogenicity at LVW1.

Representative chemicals identified by the TIE-YES approach included:

- Phthalates (plasticizers) – weak estrogen mimics
- Isosorbide dimethyl ether (carrier in cosmetics, liquid aspirin formulations) – unknown estrogenicity
- *N,N*-dibutyl formamide (industrial additive, fuel additive) – unknown estrogenicity
- Surfynol® (wetting agent, defoamer, dispersant) – unknown estrogenicity
- Butylated hydroxyanisole (food preservative, antioxidant) – weakly estrogenic
- Methyl tetradecanoate (fragrance, fabric detergents) – unknown estrogenicity
- Parsol MCX (UV-B filter in cosmetics) – potentially weakly estrogenic
- Vitamin E (antioxidant) – no estrogenic activity
- R-methyl esters – some reported as weakly estrogenic

Other chemicals not amenable to the GC-MSD method used with the TIE-YES may be present and have contributed to the measured estrogenic response.

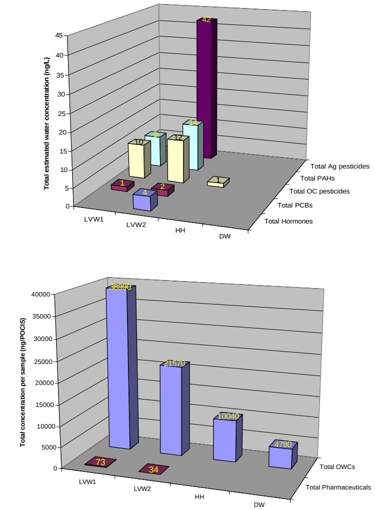

Figure 4. Relative amounts of contaminants or contaminant classes measured at each site.

OBSERVATIONS

- In general, the highest concentrations of chemicals were at the LVW2 site.
- The major OWCs detected in POCIS samples include *para*-cresol (wood preservative), *N*-butyl benzenesulfonamide (neurotoxic plasticizer used in nylon production), fragrances, phosphate flame retardants, and phthalates (plasticizers).
- Few chemicals were measured in the DW sample, generally at <0.5 ng/L.
- Total estrogenicity measured by the YES was approximately 100 times greater at LVW2 than LVW1. No estrogenicity was measured at HH or in the DW.
- The TIE-YES identified of numerous chemicals, some known to be estrogenic, in POCIS samples which are characteristic of industrial and personal-use products discharged in WWTP effluents.

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